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STATISTICAL THEORIES OF ACTIVE SURFACES

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[Figures referred to are appended.]

Introduction

In the 1920's, as a result of the work of a number of investigators, there was formulated a theory of adsorption and catalytic phenomena [1, 2], a theory usually associated with the name of Langmuir, which interpreted the then available experimental data relative to adsorption equilibria and kinetics of heterogeneous catalytic reactions. This theory is based on the following premises:

1. The surface of the adsorbent, or of the catalyst, is homogeneous throughout with respect to its adsorptive, or catalytic, properties.
2. The interaction between the adsorbed particles has practically no effect on the adsorption process as a whole.
3. The surface can be covered by no more than a monomolecular layer of the adsorptive.

Subsequently, however, experimental data were obtained which did not support these assumptions. With increasing accuracy of the experimental methods the quantity of such data increased steadily, and finally the point was reached where an agreement of the experimental results with the requirements of the theory became an exception rather than the rule.

Thus, it was found that in most instances the experimental data relating to reaction equilibrium do not satisfy the Langmuir isotherm

$$\phi(c) = \frac{ac}{1+ac} \quad \text{or} \quad \phi(c) = \frac{a}{c+b} \quad (1)$$

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where ϕ is the occupied portion of the adsorbent's surface corresponding to equilibrium concentration of the substance being adsorbed, c , and $a = 1/b$ is the adsorption coefficient. It was found that within a wide range of concentrations of solutes and gases, the experimental data often approximate more closely conditions formulated by means of the old, empirical, parabolic isotherm

$$\phi(c) = A c^\gamma \quad (2)$$

where the exponent γ is smaller than one, or by means of other, more complex derivations.

It was found further that experimental data obtained in studies of the kinetics of adsorption and heterogeneous catalytic reactions, frequently show recurring regularities which cannot be satisfactorily explained on the basis of the aforementioned theory [3-5]. Results obtained in measurements of the differential adsorption heats, which in most systems were found to vary with variation in the magnitude of surface saturation, were also in disagreement with the prevailing theory [7, 6]. Ordinarily, the greatest quantity of heat is liberated during adsorption of the very first portions of the adsorptive. The activation energy of active adsorption was also found to depend upon the degree of surface saturation; in most instances, the adsorption energy increased rapidly with increasing saturation. Analogous phenomena were observed in studies of the kinetics of contact reactions, the activation energy of these reactions varying, in many cases, with the variation in the specific saturation of the surface by reacting substances. Especially significant also were the data pertaining to catalyst poisoning. The nature of the changes in activity which take place during adsorption of the poison is frequently completely unexplainable on the basis of the aforementioned theory.

All these facts raised doubts as to the correctness of the basic postulates of the proposed theory, and prompted efforts directed toward a more satisfactory formulation of the theoretical principles involved. Three lines of approach thus suggested themselves. One may discard the hypothesis of a homogeneous surface, while retaining the other fundamental premises. One may also reject the second postulate and assume the existence of substantial forces of interaction forces between the adsorbed particles. One may finally reject the third hypothesis and assume the possibility of a multilayer adsorption. Numerous attempts were made to develop a more adequate theory along each of these lines of approach. In so far as catalytic reactions are concerned, of greatest moment are the considerations based on the rejection of the elementary theory's first postulate relating to surface homogeneity. The present publication is primarily concerned with this specific concept.

Fundamental Premises of the Theory of Heterogeneous Surfaces

It is well known that solids are actually far from being homogeneous most of them being polycrystalline and comprising small crystals of various sizes agglomerated into granules of various shapes and sizes. Deviations from stoichiometric composition are always present, as well as admixtures and extraneous adjuncts. The surface furthermore includes fissures, foramina, projections, and other flaws. The presence of such macro-heterogeneity is established by roentgenographic and electronographic data, and certain other indirect methods. In addition, it can be considered beyond doubt that heterogeneity of a more minute nature is also present, as a result of imperfect configurations of the space lattices such as deviations from interatomic distances, flaws such as voids in the lattice, inclusion of extraneous atoms, and so forth. (See, for instance, [9-12]). All these flaws and irregularities in the surface structure undoubtedly have a pronounced effect upon the field of force in the surface, causing distortions and deviations from the strict periodicity characteristic of an ideal crystalline structure. The interaction of the adsorbed molecules

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with such a heterogeneous surface will, obviously, vary at different points of the latter. Hence, the adsorption heat and activation energy depend on the area of the surface at which the process takes place. It is possible that on such a heterogeneous surface catalytic activity will not be present at all points, and that areas of catalytic activity will differ in degree of activity.

These hypotheses were suggested by many investigators, at first qualitatively, and many of them proposed certain types of surface activity, that is, adsorption or catalytic properties attributable to some specific type of disrupted structure, such as projecting atoms, voids in the space lattice, and so forth. [13-18]

All trends in the development of the theory of heterogeneous surfaces are based on the following assumed positions:

1. Different areas of the surface possess dissimilar adsorptive and catalytic characteristics.
2. Within the boundaries of a group of areas characterized by parameters of given values defining their adsorbent and catalytic properties, the elementary theory holds.

Geometrically, such a group of equivalent areas does not, of course, necessarily correspond to any isolated portion of the surface. On the contrary, a group of equivalent areas on a heterogeneous surface must be considered as the sum total of points distributed geometrically in any manner and possessing the same adsorptive and catalytic characteristics.

Thus, a process taking place on the heterogeneous surface may generally be considered as the summation of independent processes occurring on separate areas (or centers of activity). Let us consider, for instance, the adsorption equilibrium on a heterogeneous surface. Let the surface comprise areas, each of which is characterized by the inverse adsorption coefficient b within each of these areas the isotherm of Langmuir is effective:

$$\theta_m = \frac{c}{c + b_m}$$

where θ_m is the occupied portion of the surface in the area m . The occupied portion of the total heterogeneous surface is given by the sum:

$$\phi(c) = \sum_{m=1}^n \theta_m f_m = \sum_{m=1}^n \frac{f_m c}{c + b_m} \quad (3)$$

where f_m is the relative size of the area having the inverse adsorption coefficient b_m . If the number of areas having different b_m values is large, and it can be assumed that b has a continuous series of values, then the sum (3) can be replaced by the integral

$$\phi(c) = \int_{b_1}^{b_2} \frac{c}{c+b} \rho(b) db \quad (4)$$

where $\rho(b)$ is the surface's so-called distribution function relative to adsorption coefficient. This function can be determined as the derivative $\rho(b) = \frac{dS(b)}{db}$ where $S(b)$ is the portion of the surface within the boundaries of which the adsorption coefficient assumes values from zero to b .

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Therefore, $\rho(b)db$ is equal to the portion of the surface characterized by values of b lying within the limits from b to $b+db$. In other words, $\rho(b)$ represents the statistical specific weight of areas with a given b value, with respect to the total surface.

The concept of a distribution function, or more precisely, distribution density, is adopted from mathematical statistics.^[19]

In equation (4), b_1 and b_2 are respectively the least and the greatest values of b on a given surface.

In general, if any property F is dependent on a variable x , then the value of this property on a surface heterogeneous with respect to x is expressed by the integral

$$F = \int_{x_1}^{x_2} f(x) \rho(x) dx \quad (5)$$

where $f(x)$ is the dependence of the property F on x in the case of a homogeneous surface; $\rho(x)$ is the distribution function given by

$$\rho(x) = \frac{dS(x)}{dx} \quad (6)$$

and x_1 and x_2 are the minimum and the maximum values of the variable x .

If the distribution function is known, it is not difficult in principle, having calculated the integral (5), to find the corresponding law for the heterogeneous surface. Much more difficult is the converse problem of determining the distribution function $\rho(x)$ from the known law governing the property F .

The solution of both these problems in their application to adsorptive and catalytic processes was first realized by Soviet investigators, who have originated a novel statistical trend in the theory of active surfaces. This trend was initiated independently by two research teams.

S. Z. Roginskiy and coworkers (Ya. B. Zel'dovich, C. Yu. Leypunskiy, S. Yu. Yelovich and others), in making a detailed study of the stepwise behavior and kinetics of certain simple catalytic reactions, discovered the above-mentioned deviations from the Langmuir theory in processes involving the adsorption and catalytic oxidation of carbon monoxide on manganese dioxide, the adsorption of hydrogen and catalytic hydrogenation of hydrocarbons on nickel, copper, etc. In order to explain these anomalies, they proposed the concept of heterogeneity of the active surfaces, and formulated the experimentally derived relations by introducing the distribution function (6) comprising the suitable parameters. These researches progressed over a period of years, and culminated in the creation of a general theory governing processes on heterogeneous surfaces. This theory was developed by Roginskiy.

Quite independently, A. N. Frumkin and his collaborators, (M. I. Temkin, M. Shlygin, R. Kh. Burshtein, and others), discovered a number of anomalous properties displayed by active surfaces. Specifically, the study of polarization of metallic electrodes led them to the discovery of an unusual logarithmic adsorption isotherm, which was given a theoretical basis by means of a representation concerning surface heterogeneity. Results of studies of para-ortho conversion of hydrogen and other processes suggested surface heterogeneity. Frumkin and associates undertook a vast number of theoretical researches in connection with adsorption and catalysis on heterogeneous surfaces, which were conducted primarily by M. I. Temkin.

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More recently, substantial contributions to the statistical theory of adsorption phenomena were made by M. M. Dubinin and his collaborators, whose work we will not discuss here, since it pertains to a field beyond the scope of our consideration.

The Adsorption Equilibrium

Langmuir had already discussed the possibility of considering the adsorption process on a surface as a result of a summation of independent processes on homogeneous areas, and proposed the schematic formula

$$q(p) = \sum_i \frac{a_i p}{p + b_i}$$

wherein $q(p)$ is the amount of substance adsorbed at equilibrium, at a pressure p . [20]

However, neither Langmuir himself nor his numerous followers advanced beyond this general formula or reached any further conclusions, and essentially they merely formulated the problem in a most general manner. In connection with adsorption equilibrium, the first investigator who initiated a statistical treatment of heterogeneous surfaces of adsorbents was the Soviet scientist Zel'dovich, who at that time was working in Roginskiy's laboratory. [21] Zel'dovich undertook specifically a theoretical study of the problem concerning the possible origin of the parabolic isotherm (2), which is so frequently encountered in experimental work. He demonstrated that this function may result from heterogeneity of the adsorbent, and should occur on surfaces characterized by an exponential distribution function of adsorption heat.

$$\rho(Q) = C e^{-\alpha Q} \quad (7)$$

where Q is the heat of adsorption, while C and α are constants.

Using formula (4) as the isotherm of heterogeneous surfaces, Zel'dovich utilized the following method for determining approximately function $\rho(b)$ for a given $Q(p)$, that is, for solving integral (4).

The Langmuir isotherm is replaced by two straight lines: $\phi(p) = \frac{p}{b}$ where $0 < p < b$, and $\phi(p) = 1$ where $p > b$. Then, if $b_1 = 0$ and $b_2 = b_0$, we have

$$\phi(p) \approx \int_0^p \rho(b) db + p \int_p^{b_0} \frac{\rho(b)}{b} db \quad (8)$$

On successive differentiation with respect to p , equation (8) yields the desired solution

$$\rho(b) = -b \left(\frac{d^2 \phi(p)}{d p^2} \right)_{p=b} \quad (9)$$

On applying formula (9) to the parabolic isotherm (2), we obtain

$$\rho(b) \approx \frac{1}{2} \gamma (1 - \gamma) b^{\gamma-1} = A b^{\gamma-1}$$

Substitution of the function $\rho(b)$ thus obtained, in the initial integral (4), gives

$$\phi(p) = A' p \int_0^{b_0} \frac{b^{\gamma-1} db}{p+b} \quad (10)$$

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When $p \ll b_0$ and $\gamma < 1$, equation (10) gives the limit value of $\phi(p)$

$$\lim_{p \rightarrow 0} \phi(p) = \frac{A' \pi}{\sin \gamma \pi} \cdot p^\gamma = A p^\gamma$$

that is, the parabolic isotherm (2). Since formula (9) determines $\rho(b)$ only within the accuracy of a constant coefficient, the value of A' is determined from the condition of normalization:

$$\int_0^{b_0} \rho(b) db = 1$$

which gives $A' = \gamma b_0^{-\gamma}$

In order to obtain distribution function in adsorption heats, we use the following obvious equations:

$$\rho(Q) dQ = \rho(b) db; \quad b = b_0 e^{-Q/RT}$$

Hence, assuming that b_0 is independent of Q , the function $\rho(Q)$ is equal to

$$\rho(Q) = \frac{\gamma}{RT} e^{-\gamma Q/RT} = C e^{-\alpha Q}$$

where $C = \alpha = \gamma/RT$

An analogous study was made several years later by Cremer and Fluegge, who assumed that the active adsorption centers are voids in the space lattice of the order of atomic dimensions. [22] They further assumed that these voids are formed as a result of thermal motion at the temperature of preparation of the catalyst or adsorbent, and that the equilibrium attained at this temperature is retained or "frozen" on subsequent cooling. The probability of the formation of a void in the lattice at a temperature T is proportional to the value $e^{-E/T}$, E being the energy expended in the formation of the void. Since the distribution occurring at temperature T is retained on cooling, the portion of active centers having an excess of energy E , that is, the distribution function in E , is equal to:

$$\rho(E) = \text{Const.} \cdot e^{-E/RT}$$

On assuming further that E is equal to the adsorption heat (?) [sic], the authors obtain the following isotherm of heterogeneous surfaces:

$$\phi(p) = \text{Const.} \cdot p \int_{Q_0}^{\infty} \frac{e^{-Q/RT} dQ}{p+b}$$

For low pressures and b_0 constant, this express is approximately equal to

$$\phi(p) = \text{Const.} \frac{\gamma \pi}{\sin \pi (1-\gamma)} \cdot p^\gamma = A p^\gamma$$

wherein $\gamma = \frac{T}{T_0}$ the result being within the value of the constant, the same as that obtained by Zel'dovich.

It is regrettable that Cremer and Fluegge fail to mention the work of Zel'dovich, even though the latter had been published in 1935.

The next substantial contribution to the development of the statistical theory were the researches of Temkin [23], who, having proposed a uniform distribution of the surface in adsorption heats,

$$\rho(Q) = \text{Const.} \quad (11)$$

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substantiated from a theoretical standpoint the adsorption isotherm

$$\Phi(p) = C_1 \lg(a_p) \quad (12)$$

which was empirically derived by Frumkin and Shlygin. [24] If we assume the uniform distribution (11), integral (4) becomes

$$\Phi(p) = \frac{RT}{C} \ln \frac{1+a_0 p}{1+a_1 p}; \quad a_1 = a_0 e^{-C/RT} = a_0 e^{-1} \quad (13)$$

wherein $a_0 = 1/b_0$. At pressures such that $a_1 p \gg 1$, and $a_1 p \ll 1$ (in the so-called zone of medium saturation), (13) approximates the following expression

$$\Phi(p) = -\frac{1}{f} \ln a_0 p \quad (14)$$

which coincides with (12).

Further development of the theory of heterogeneous surfaces was hampered by certain mathematical difficulties. Solution of integrals of the form (5) in many cases either is impossible by means of elementary functions or results in cumbersome, complex formulas. The problem becomes especially arduous when it is necessary to determine the unknown function $f(x)$ on the basis of the known function F , which requires the solution of integral equations of the following type

$$F(t) = \int_a^b f(x, t) f(x) dx$$

which, in general, is most complex. Therefore, it was deemed more expedient to introduce simplifications without unduly distorting the general physical picture of the prevailing physical conditions, while readily allowing for clear relations of a general nature which admit experimental verification. One of these simplifications, in the case of adsorption equilibrium, is the formula of Zel'dovich (9).

Roginskiy proposed a simplified analytical method for studying processes on heterogeneous surfaces [25-29], which is applicable not only to adsorption equilibrium but also to many other statistical problems.

The simplicity and lucidity of this method enabled Roginskiy to develop an orderly theory of processes on heterogeneous surfaces, which affords a simple interpretation of a number of hitherto unexplainable phenomena.

In its application to adsorption equilibrium, the gist of Roginskiy's method is as follows. According to the foregoing considerations, the adsorption isotherm on a heterogeneous surface is given by the equation:

$$\Phi(p) = \int_{a_1}^{a_2} \frac{p f(Q) dQ}{p + b_0 e^{-Q/RT}} \quad (15)$$

Let us express $f(Q)$ in fractions of unity, i.e.,

$$\int_{a_1}^{a_2} f(Q) dQ = 1$$

Let us assume b_0 to be independent of Q , and plot the graph of the function

$$\theta(Q) = \frac{p}{p + b_0 e^{-Q/RT}}$$

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Figure 1 shows that $\theta(Q)$ has an inflection point whose abscissa, as can be readily ascertained, is

$$Q_{inf} = RT \cdot \ln b_0 / p \quad (16)$$

and whose ordinate is $\theta_{inf} = \frac{1}{2} [\theta_{inf} \text{ means } \theta \text{ inflection}]$

Let us consider distribution function $p(Q)$ shown in Figure 2. On the same graph is also plotted the curve of the function $\theta(Q) \cdot p(Q)$, the shaded area enclosed by this curve, the axis of abscissae, and the ordinates Q_1 and Q_2 , is equal to the integral (15). This area can be replaced by the equal area ΔBQ_2Q_{gr} which is equivalent to substituting for the integral (15), the equal integral

$$\phi(p) = \int_{Q_{gr}}^{Q_2} p(Q) dQ \quad [Q_{gr} \text{ stands for } Q_{graph}]$$

In virtue of the steeply ascending slope of curve $\theta(Q) \cdot p(Q)$ for steadily and slowly changing function $p(Q)$, and for sufficiently wide interval between Q_1 and Q_2 , it may be assumed approximately that the point Q_{gr} coincides with the abscissa of the inflection point of the curve $\theta(Q)$:

$$Q_{gr} \approx Q_{inf} = RT \cdot \ln b_0 / p$$

The adsorption isotherm can then be written as follows:

$$\phi(p) = \int_{Q_{inf} = RT \cdot \ln b_0 / p}^{Q_2} p(Q) dQ \quad (17)$$

Thus, all areas of the surface having adsorption heats greater than Q_{inf} are practically completely occupied ($\theta = 1$), while all areas of the surface with adsorption heats less than θ_{inf} , are practically free of the adsorptive ($\theta \approx 0$).

The formula (17) thus obtained can be used to determine the adsorption isotherms corresponding to uniform $[p(Q) = \text{const}]$, and exponential $[p(Q) = Ce^{-\alpha Q}]$ distribution by adsorption heats. The computations in these cases give:

$$Q(p) = \text{const} (Q_2 - RT \cdot \ln b_0 + RT \ln p) = C_1 + C_2 \lg p$$

and

$$\phi(p) = \frac{c}{\alpha} \left(\frac{p}{b_0} \right)^{\alpha RT} - \frac{c}{\alpha} e^{-\alpha Q_2} = C_1 p^\gamma - c_2'$$

which, within the accuracy of the constants, is in agreement with the results obtained by other authors on using more rigorous but also more complicated procedures. The originator of this method has studied a number of other isotherms corresponding to linear, hyperbolic, and stepwise distribution. The use of Roginskiy's method greatly simplifies the task of determining the distribution function $p(Q)$ on the basis of the known isotherm $\phi(p)$. Differentiation of (17) with respect to the lower limit gives:

$$p(Q_{inf}) = -\frac{d\phi}{dQ_{inf}} = -\left(\frac{d\phi}{dp} \cdot \frac{dp}{dQ_{inf}} \right) = p/RT \cdot \frac{d\phi}{dp} = \frac{1}{RT} \left[\frac{d\phi}{d \ln p} \right]_{p = b_0 e^{-Q_{inf}/RT}} \quad (18)$$

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By means of this very simple expression, the form of function $\rho(Q)$ can be readily determined from experimental data, since $\frac{d\phi}{dQ_{inf}}$ can be readily found, graphically for example. The value of b_0 can also be found without difficulty. From (17) it follows that to two equal values of ϕ , for different temperatures T_1 and T_2 , correspond equal values of Q_{inf} , and thus we obtain from (16)

$$\lg b_0 = \frac{T_1 \lg p_1 - T_2 \lg p_2}{T_1 - T_2}$$

Function $\rho(Q)$ can be found not only from the isotherm, but also on the basis of a known adsorption isobar. According to the theory of Roginskiy, when $p = \text{const}$ we have the following relation:

$$Q_{inf} = RT(\ln b_0 - \ln p) = CT$$

and therefore the isobar equation has the form

$$\phi(T)_p \approx \int_{Q_{inf}=CT}^{Q_2} \rho(Q) dQ$$

and the distribution function is determined by means of the formula:

$$\rho(Q) = \frac{dQ}{dQ_{inf}} = - \frac{1}{C} \left[\frac{dQ(T)}{dT} \right]_{T = \frac{Q_{inf}}{C}}$$

The differential adsorption heats can be determined just as readily. By definition, the differential heat of adsorption is equal to

$$Q_{diff} = \frac{dG}{d\phi}$$

where G is the total thermal effect on the entire surface, an effect corresponding to the degree of saturation ϕ . On a heterogeneous surface, however, we have

$$G = \int_{Q_1}^{Q_2} Q \cdot \theta(Q) \cdot \rho(Q) dQ \approx \int_{Q_{inf}}^{Q_2} Q \rho(Q) dQ$$

and therefore Q_{diff} is equal to

$$Q_{diff} = \frac{dG}{d\phi} = \frac{dG}{dQ_{inf}} \frac{dQ_{inf}}{d\phi} = \frac{d}{dQ_{inf}} \int_{Q_{inf}}^{Q_2} Q \rho(Q) dQ$$

This method of analyzing processes on heterogeneous surfaces was applied by Roginskiy not only to adsorption and desorption equilibria but also to the kinetics of adsorption and contact reactions and also to catalyst poisoning (see below). A complete presentation of the method and its applications, including examples showing analyses of experimental data, is given in a special monograph.^[29] It must be pointed out that the device utilized by Roginskiy is one of broad significance and is applicable not only to problems of adsorption and catalysis; it may be regarded as an approximate method for solving integral equations of the type:

$$F(x) = \int_d^b h(x, t) f(t) dt$$

in which the kernel $h(x, t)$ displays the following characteristics:

$$h(x, t) \approx C_1 \text{ when } t < t_1$$

$$h(x, t) \approx C_2 \text{ when } t > t_2$$

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$h(x, t)$ is a continuous function having no maximum or minimum

The main variation of $h(x, t)$, from $h \approx C_1$ to $h \approx C_2$ occurs in the interval (t_1, t_2) . The function $f(t)$ is given in the interval (t_{\min}, t_{\max}) where $t_{\min} \ll t_1$ and $t_{\max} \ll t_2$, and $f(t)$ varies relatively slowly and steadily within this interval.

Thus, the method of Roginskiy is applicable to the solution of all problems which satisfy the above conditions. When $f(t) = \text{const}$, the method yields altogether accurate results; in all other instances, the accuracy is inversely proportional to the relative variation of $f(t)$ within the interval (t_1, t_2) .

In spite of its versatility, the method is, of course, not applicable where the above-stated conditions are not met; for instance, if $f(t)$ undergoes wide variations within the interval (t_1, t_2) . Hence, it was necessary to develop still other methods which are not subject to such limitations.

The investigations of Temkin and Levich [31], and of Todes and Bondareva [32], are devoted to this problem in its application to adsorption equilibrium.

Temkin and Levich introduce the variables $\chi = \ln p$ and $\xi = \ln b$ and, setting $b_1 = 0$ and $b_2 = \infty$ in (4), obtain the equation

$$\phi(\chi) = \int_{-\infty}^{+\infty} \frac{\rho(\xi) d\xi}{1 + e^{\xi - \chi}}$$

the solution of which (see, for example, V. I. Smirnov, Advanced Mathematics, Vol 4) is the function

$$\rho(\xi) = \frac{1}{2\pi i} \left[\phi(\chi + \pi i) - \phi(\chi - \pi i) \right]_{\chi = \xi} \quad (19)$$

On the basis of this solution, Temkin and Levich have studied the empirical isotherms, previously analyzed by Zel'dovich and Roginskiy, and have obtained, in most instances, results closely approximating those obtained by the latter authors. It must be pointed out that, strictly speaking, solution (19) can be applied to a function $\phi(x)$ only if this function satisfies a number of specific conditions, which are not met by most empirical formulas commonly utilized in the approximation of experimentally derived isotherms. For this reason, the results obtained by Temkin and Levich during analysis of certain empirical isotherms are not rigorous, and hence do not afford any appreciable advantage over results obtained by approximate methods.

The use of formula (19) is not expedient for a direct determination of $\rho(\xi)$ from experimental data, since it contains the function of a complex argument. Therefore, the above-named investigators have formulated (19) as a series:

$$\rho(\xi) = \left[\phi'(\chi) - \frac{\pi^2}{3!} \phi'''(\chi) + \frac{\pi^4}{5!} \phi^{(5)}(\chi) - \dots \right]_{\chi = \xi} \quad (19a)$$

However, the application of this series is also laborious, because of the difficulty of determining the higher order derivatives of $\phi(x)$ on the basis of experimental data.

Todes and Bondareva studied a number of rigorous, asymptotic methods for solving the same problem. One of these methods is the following: The function $\phi(P)$ is formulated as the series

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$$\phi(p) = 1 - \frac{C_1}{p} + \frac{C_2}{p^2} - \dots + \frac{C_k}{p^k}$$

which in turn is approximated by the polynomial

$$\phi(p) = 1 - \sum_{m=i} \frac{C_m}{p^m}$$

The desired function $\phi(x)$ is formulated as a sum of Laguerre functions

$$\rho(b) = e^{-b} \sum_{m=0}^{\infty} \frac{\rho_m}{(m!)^2} \cdot L_m(b), \quad L_m(b) = \sum_{k=0}^m (-1)^k \frac{(m!)^2}{(k!)^2 (m-k)!} b^k \quad (20)$$

The coefficients ρ_m and C_k are related as follows:

$$\rho_m = \sum_{k=0}^m (-1)^k \frac{(m!)^2}{(k!)^2 (m-k)!} C_k \quad (20a)$$

Todes and Bondareva determined the conditions that must be fulfilled by the approximate function $\phi(p)$ in order to render it suitable for the determination of $\rho(\xi)$ from formulas (19), (20), or the like.

It must be pointed out that although the equations (19), (19a), (20), (20a), and others adduced in the above-mentioned studies are obtained by quite rigorous methods, their practical applications necessitate the introduction of a number of additional simplifications which greatly detract from the accuracy of the results so obtained. In addition, the very application of these equations was found to be most cumbersome and complex. Hence, the method of Roginskiy is much to be preferred as being considerably simpler and more serviceable in all instances where the problem involved permits its utilization.

The foregoing discussion relates to the adsorption of but a single substance. The adsorption of various mixtures on heterogeneous surfaces was studied by Roginskiy and Todes [33], by utilizing the above-described method of Roginskiy. These authors studied in detail the adsorption of a mixture of two substances, for the case of a linear dependence between the adsorption heats of the mixed components, as well as for the case of the absence of a dependence between these quantities, and thus derived adsorption isotherms of the mixed components expressed by means of the isotherms of the pure substances.

It is known that for adsorption of a gaseous mixture on a homogeneous surface, the degree of saturation by the i -th gas is given by the equation

$$Q_i = \frac{C_i/b_i}{1 + \sum_j C_j/b_j} \quad (21)$$

where the summation $\sum_j C_j/b_j$ is effected with respect to all components of the mixture. It follows from (21) that the ratio Δ of the fractions of saturation of the two components on a homogeneous surface or on a homogeneous area of a heterogeneous surface is equal to

$$\Delta = \frac{\theta_i}{\theta_k} = \frac{C_i}{C_k} \cdot \frac{b_k}{b_i} = \frac{C_i}{C_k} \cdot \frac{b_{ok}}{b_{oi}} \exp \left[\frac{Q_i - Q_k}{RT} \right] \quad (22)$$

According to Roginskiy and Todes, the nature of the adsorption equilibrium of a mixture on a heterogeneous surface is determined by the functional interrelation between the adsorption heats of the mixed components on the same area.

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In the presence of such interrelation, on transition from one area to another the adsorption heat Q_k of gas k will vary, depending on the adsorption heat Q_1 of gas k :

$$Q_k = f(Q_1)$$

Let us take as an example the case studied by Roginskiy and Todes, where Q_k and Q_1 are directly proportional

$$Q_k = \beta_{ik} Q_1 \quad (23)$$

Such an interrelation may be expected in the case of adsorption brought about by dispersive or electrostatic forces. In the first instance (dispersive interaction), we have

$$\beta_{ik} \sim \frac{\alpha_k}{\alpha_i} \sim \sqrt{\frac{a_k}{a_i}} \sim \sqrt{\frac{T_{kp} k}{T_{kp} i}}$$

where α is the polarizability of the gas molecule, a is Van der Waals' constant, and T_{kp} is the critical temperature. In the second instance (electrostatic interaction), for adsorption of dipolar molecules we have

$$\beta_{ik} \sim \left(\frac{\mu_k}{\mu_i}\right)^2$$

where μ is the dipole moment of the molecule.

Taking into consideration (23), the expression (22) becomes, in the case of a mixture of two gases,

$$\Delta = \frac{\theta_2}{\theta_1} = \frac{C_2}{C_1} \cdot \frac{b_{02}}{b_{01}} \exp \left[\frac{Q_1 (1-\beta)}{RT} \right] \quad (24)$$

It is apparent, therefore, that for $\beta < 1$, if the concentrations of both substances are of the same order, and the more so if $C_2 > C_1$, then on the overwhelming majority of surface areas we have $\theta_2 > \theta_1$, that is, practically only one of the substances is being adsorbed. In this case, the presence of the first component does not affect the adsorption of the second component. It may happen, however, that $C_1 \ll C_2$. In such a case, both substances will be adsorbed, and in view of the sharp (exponential) dependence of A on Q_1 , for values of Q_1 less than a certain value Q_1^* ,

$$Q_1 = Q_1^* = \frac{RT}{1-\beta} \ln \frac{C_1 b_{02}}{C_2 b_{01}}$$

Practically only one of the substances, namely the first gas, will be present on the surface; whereas, if $Q_1 > Q_1^*$ only the second gas will be present. This relation is shown in Figure 3A, where the area I corresponds to the portion of the surface occupied by the first gas, and the area II corresponds to that part occupied by the second gas. Under these conditions, the adsorption of the first gas is equal to

$$\phi_1(C_1, C_2) \approx \int_{Q_1^*}^{Q_1^*} P(Q_1) dQ_1 \quad (25a)$$

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and that of the second gas

$$\phi_2(c_1, c_2) \approx \int_{a_i^*}^{a_i^{max}} p(a_i) da_i \quad (25b)$$

The total adsorption of both substances is thus equal to:

$$\phi(c_1, c_2) = \int_{a_i^*}^{a_i^{max}} p(a_i) da_i + \int_{a_i^*}^{a_i^{max}} p(a_i) da_i = \int_{a_i^*}^{a_i^{max}} p(a_i) da_i \quad (25c)$$

In addition to the above discussed sybatic variations of the adsorption heats of the mixed components, there can also exist an antibatic dependence between these quantities. In the latter case, which we shall not discuss here in detail, the areas having the highest adsorption heats with respect to one of the gases are those having the lowest adsorption heats, in so far as the other gas is concerned. As a result both gases are adsorbed quite independently up to the point where the partial pressures of both components and their ratio reach definite critical values corresponding to a complete occupation of the surface, whereupon no further adsorption will take place. Figure 3B represents the adsorption of a mixture of two gases with antibatic Q_1 and Q_2 , in the case of partial occupation of the surface; and Figure 3C in the case of complete occupation of the surface.

It is noteworthy that the adsorption isotherms of mixed components can always be determined approximately on the basis of the theory of Roginskiy and Todes, if the adsorption isotherms of the pure substances are known. Thus, it is apparent from the foregoing considerations that in the case of sybatic Q_1 and Q_2 , if C_2 and C_1 are quantities of the same order, only one, namely the second gas, is being adsorbed and the adsorption isotherm obviously will coincide with that of this second gas in its pure state. If, on the other hand, $C_2 \ll C_1$, then the adsorption isotherm of each component and the summative isotherm derived by means of formulas (25) can be expressed on the basis of the adsorption isotherms of the pure substances:

$$\phi_1(c_1, c_2) = \int_{a_i^*}^{a_i^{max}} p(a_i) da_i = \int_{a_i^*}^{a_i^{max}} p(a_i) da_i - \int_{a_i^*}^{a_i^{max}} p(a_i) da_i = \phi_1^*(c_1) - \phi_1^*(c_1^*)$$

$$\phi_2(c_1, c_2) = \int_{a_i^*}^{a_i^{max}} p(a_i) da_i = \phi_1^*(c_1^*)$$

$$\text{and } Q(c_1, c_2) = \phi_1(c_1, c_2) + \phi_2(c_1, c_2) = \int_{a_i^*}^{a_i^{max}} p(a_i) da_i = \phi_1^*(c_1)$$

where $Q^*(c_1)$ is the adsorption isotherm of the first gas in its pure state. The interrelations between the isotherms of adsorption of mixtures of pure substances, can be determined just as readily in the case of antibatic Q_1 and Q_2 , and in the absence of a dependence between Q_1 and Q_2 .

The statistical theory of processes on heterogeneous surfaces was established and studied in detail almost exclusively as a result of the endeavors of Soviet scientists. The scanty researches in this field which were conducted abroad are, with few exceptions, less significant than Soviet work from a scientific standpoint. They are on a lower theoretical plane than Soviet works. Thus, it appears the more surprising that some of the foreign investigators, in publishing papers dealing with statistics of heterogeneous surfaces, ignore the work of the Soviet scientists who established the fundamentals in this field, even when the contents of such foreign publications are substantially a duplication of prior Soviet researches.

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Thus, in 1938 Cremer and Fluegge published a paper [22] devoted to the statistical interpretation of the parabolic isotherm, without referring to the scientifically much more significant publication of Zel'dovich, which had appeared 3 years earlier in German, the native tongue of Cremer and Fluegge.

More recently the eminent American physical chemist, H. S. Taylor, published a paper devoted essentially to the statistical derivation of the same parabolic and logarithmic isotherms. [39] Taylor also fails to mention the numerous publications of Soviet scientists who had formulated the same fundamental principles from 5 to 12 years earlier. Incidentally, some of these prior publications appeared in Taylor's native language.

Taylor's publication, however, does not compare favorably with the thorough investigations of Zel'dovich, Temkin, and others, which were conducted on a much higher physical and mathematical level.

Taylor derives the logarithmic isotherm on the basis of uniform homogeneous distribution, as was done by Temkin in 1941, and the parabolic isotherm on the basis of exponential distribution, as Zel'dovich had done in 1935. In this latter case, however, Taylor assumes the existence, on the surface, of areas having large negative adsorption heat values (integration with respect to Q up to $-\infty$), which does not appear to be sound physics. Furthermore, in order to determine the function $\rho(Q)$ corresponding to experimental observations, he proceeds by the cut-and-try method of applying one type of function after another, whereas Soviet scientists had long since developed general methods for determining the form of $\rho(Q)$ directly from experimental data. The specific results obtained by Taylor from analyzing data relating to hydrogen adsorption on tungsten are also not novel. This problem had been investigated more thoroughly by Roginskiy, by his own method.

Thus, by such disregard of Soviet researches, Taylor appears in the ludicrous position of a man who is discovering well known facts.

Adsorption Kinetics

The nature of adsorption kinetics on a heterogeneous surface was shown by Roginskiy [26, 30] to depend on whether the molecules remain at the points where they initially came in contact with the surface during the process (adsorption without redistribution), or undergo redistribution on the surface in accordance with the values of the adsorption coefficients on different areas of the surface. In the latter case, the factor determining the kinetics is in the nature of a functional relationship between activation energy and adsorption heat on the same area of the surface. Let us consider the possible basic variants of the process, according to Roginskiy

a. Adsorption without redistribution. In this case, because of the random collision of molecules upon the surface and the absence of any lateral movement of the adsorbed molecules on the surface, the velocity of the process is determined solely by surface distribution with respect to activation energies, irrespective of distribution by adsorption heats. The velocity on an area with a given value of activation energy is expressed by the differential equation:

$$\frac{d\theta}{dt} = K_0 e^{-E/RT} p(i-\theta) \quad (26)$$

Integration of (26), at a constant pressure, gives

$$1-\theta = \exp \left[-K_0 p t \cdot e^{-E/RT} \right] \quad (27)$$

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Equation (27) defines the portion of unoccupied (free) surface on the area having the activation energy E at the time t . The portion ψ of the free surface at the time t is given by the integral

$$\psi(t) = 1 - \phi(t) = \int_{E_1}^{E_2} \exp[-K_0 p t e^{-E/RT}] \rho(E) dE \quad (28)$$

where $\rho(E)$ is the function of surface distribution in activation energies, while E_1 and E_2 are the minimum and maximum values of the activation energy on the surface.

b. Adsorption with redistribution in the absence of functional relation between E and Q . An area having a given value of activation energy can possess an adsorption heat of any magnitude. As a result of redistribution (the velocity of which is assumed to be considerably greater than that of adsorption), different areas of the surface undergo saturation in proportion to decreasing heats of adsorption, and at any point of time, areas having any value of activation energy, from maximum to minimum, will participate in the process. In view of the exponential law of dependence of velocity on activation energy, the velocity will actually be determined by processes occurring on areas having minimum E values. On the graph $\rho(E)$, these areas constitute a relatively narrow vertical strip, the location of which determines the velocity of the process. This strip is referred to as the controlling band (Figure 4). With increasing saturation of the surface, the controlling band, while remaining stationary, decreases in height; i.e., the number of areas with low activation energy decreases steadily and the velocity of the summative process declines, because of the elimination of the saturated areas. The expression giving the adsorption velocity on the total surface is

$$\frac{d\phi}{dt} = K_0 p e^{-\frac{E_{min}}{RT}} (1 - \phi) \cdot \rho(E_{min}) = K_0 e^{-\frac{E_{min}}{RT}} (1 - \phi) \quad (29)$$

In this instance, the activation energy of the summative process is independent of saturation (the same as in the case of a strictly homogeneous surface), and the kinetics thus formally coincides with that of a homogeneous surface.

c. E and Q vary symbatically; that is, as Q increases from one area to another, E also increases. In such a case, the velocity will also be determined by the process occurring on areas having minimum activation energies, which areas will, however, remain practically uncovered almost up to the complete saturation of the surface, since redistribution will cause migration of the molecules adsorbed on these areas onto areas having higher heats of adsorption. The controlling band in this case, too, is stationary but does not undergo any alteration in height almost to the very end of the process, the velocity of which on the total surface will be constant and of zero order (Figure 5).

$$\frac{d\phi}{dt} = K_0 p \cdot \rho(E_{min}) e^{-\frac{E_{min}}{RT}} = K_0 e^{-\frac{E_{min}}{RT}} \quad (30)$$

d. E and Q vary antipatically, that is, with increasing Q , E decreases. The areas having the lowest activation energy are at the same time those having the greatest adsorption heat. Consequently, the occurrence of redistribution does not affect the velocity of the process. With increasing saturation, the controlling band moves toward higher E values (Figure 6). The kinetics in this case practically coincides with the kinetics of the previously discussed process without redistribution.

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Temkin [23] has formulated equations for the kinetics of adsorption on a surface with uniform distribution in activation energies and a linear dependence between activation energy and adsorption heat. On the basis of the fact that in many similar reactions, the variation in activation energy during transition from one reaction to another constitutes a certain definite fraction of the thermal effect, Temkin assumed that this rule holds in the case of the adsorption process and that the activation energy decreases with increasing adsorption heat, in accordance with

$$E = E_0 - \alpha Q \quad (31)$$

where E_0 and α are constants. Equation (26) thus becomes

$$\frac{d\theta}{dt} = K_0 e^{-E(Q)/RT} \cdot p [1 - \theta(Q)]$$

For the entire surface the velocity is equal to

$$\frac{d\phi}{dt} = \int_{Q_0}^{Q_1} K_0 e^{-E(Q)/RT} \cdot p [1 - \theta(Q)] \rho(Q) dQ$$

Assuming that the function $E(Q)$ is given by equation (31), and that K_0 is independent of Q , Temkin obtained a somewhat complex and cumbersome expression which, within the limits of medium saturations, can be approximately represented by the formula.

$$\frac{d\phi}{dt} = \frac{K' p}{(\alpha_0 p)^\alpha} \quad (32)$$

or, on taking into consideration (14),

$$\frac{d\phi}{dt} = K' p e^{-g\phi} \quad (33)$$

wherein $g = \alpha f$.

The kinetic equation (33) was originally obtained empirically by Roginskiy and Zel'dovich [24] and subsequently was substantiated repeatedly by experimental results. Its relation with the uniform distribution was demonstrated by Yelovich and Kharekhorin [25], who studied, not $\rho(E)$, but the function

$$E(\phi) = E_0 + \alpha \phi \quad (34)$$

However, from (34), $\rho(E)$ can be derived by means of formula (6)

$$\rho(E) = \frac{d\phi}{dE} = \frac{1}{\alpha} = \text{const}$$

The desorption velocity, according to Temkin, is given by the equation

$$-\frac{d\phi}{dt} = K'' e^{-h\phi} \quad (34a)$$

Roginskiy, using his approximate method, made a study of the general aspects of adsorption and desorption kinetics. By utilizing a simplification analogous to that which he had introduced in the study of the theory of adsorption equilibrium, he obtained in the case of adsorption without redistribution, or with redistribution and antitactic E and Q , the following approximate expression:

$$\psi(t) = \int_{E_1}^{E_{inf} = RT \cdot \ln K_0 p t} f(E) dE \quad (35)$$

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Formula (35) gives, in the case of a uniform distribution $\rho(E) = \text{Const}$, the kinetic isotherm

$$\phi(t) = a \ln t + C \text{ or } \frac{d\phi}{dt} = a'e^{-a\phi}$$

In the case of an exponential distribution, the following equation is obtained:

$$\phi(t) = A \cdot t^k$$

which is also very frequently encountered experimentally.

In the desorption process, the following relation takes place:

$$\psi(t) = \int_{E_1}^{E_{inf} = RT \ln K_0 t} \rho(E_{des}) dE_{des}$$

The kinetics of processes involving the adsorption of mixtures, which we shall not discuss here, is dealt with in detail in the previously mentioned monograph by Roginskiy. [29]

According to Roginskiy, the unknown distribution function is determined on the basis of kinetic data by means of the following formulas:

$$\rho(E) = \frac{1}{RT} \left[\frac{d\phi(t)}{d \ln t} \right] = \left[\frac{t}{RT} \cdot \frac{d\phi(t)}{dt} \right]_{t=(1/K_0 p) \exp(E/RT)}$$

$$\rho(E_{des}) = \frac{1}{RT} \left[\frac{d\psi(t)}{d \ln t} \right] = \left[\frac{t}{RT} \cdot \frac{d\psi(t)}{dt} \right]_{t=(1/K_0) \exp(E_{des}/RT)}$$

Thus, for example, the kinetic equation

$$\phi = [a \ln t]^2$$

corresponds to the distribution function

$$\rho(E) = \frac{2a^2}{(RT)^2} [E - RT \ln K_0] = A(E - B)$$

It is of interest to note that according to Roginskiy's theory, the laws governing the equilibrium and the kinetics of adsorption on heterogeneous surfaces are very much alike formally.

If we substitute K_0 for b_0 , and t for p in the equilibrium formulas, the corresponding kinetic formulas are obtained. This indicates that in processes determined by quantities having no constant values but distributed in accordance with some statistical law, the effect of the latter has such a pronounced influence on the process that it may become its determining factor. In other words, the formal expression of the recurring regularities is determined, primarily, by the form of the distribution function.

For an accurate solution of the problem of determining the distribution function $\rho(E)$ in activation energies E , the present author has suggested a method [35] which is free of the limitations inherent in the method of Roginskiy.

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Let us first solve the integral equation (28) in the general form. Let us assume in (29) $E_1=0, E_2=\infty$, and introduce the variables $y=ln t$ and $y'=E/RT$. Thus, we obtain

$$\psi(e^y) = \psi(y) = \int_0^{\infty} \exp[-K'_0 e^{y-x}] \rho(x) dx \quad (36)$$

wherein $K'_0 = K_0 \rho$.

On multiplying both members of (36) by $e^{-sy} dy$ and integrating from

$$-\infty \text{ to } +\infty, \text{ we get } \int_{-\infty}^{+\infty} e^{-sy} \psi(y) dy = \int_{-\infty}^{+\infty} e^{-sy} dy \int_0^{\infty} \exp[-K'_0 e^{y-x}] \rho(x) dx \quad (37)$$

It can be shown that the integral

$$\int_0^{\infty} \exp[-K'_0 e^{y-x}] \rho(x) dx$$

converges uniformly in the parameter y . Hence, we can change the order of integration and having done so wherever possible, we have

$$\int_{-\infty}^{+\infty} e^{-sy} \phi(y) dy = K'_0 \int_0^{\infty} e^{-sx} \rho(x) dx$$

provided the real part of s is less than zero [$\Gamma(-s)$ is the gamma function]. It can be further shown that the expression

$$Y(s) = \int_{-\infty}^{+\infty} e^{-sy} \phi(y) dy, \quad R(s) = \int_0^{\infty} e^{-sx} \rho(x) dx \quad (38)$$

can be considered as the Laplace transforms of function $\phi(y)$ and $\rho(x)$. [See, for example, V. I. Smirnov, Advanced Mathematics, Vol 4].

$$\text{Thus} \quad Y(s) = K'_0 \Gamma(-s) R(s) \quad (39)$$

From (39), by conversion of the Laplace transform we obtain $\rho(x)$ as the integral

$$\rho(x) = \frac{1}{2\pi i} \int_{\sigma-i\infty}^{\sigma+i\infty} \frac{e^{sx} Y(s) ds}{K'_0 \Gamma(-s)} \quad (40)$$

where $s = \sigma + i\tau$ is a complex variable, and integration is effected on a straight line parallel to the imaginary axis $\sigma = \text{const}$, where σ is a real number within the interval $-\infty < \sigma < 0$ (see Smirnov, loc. cit.).

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To compute $Y(s)$ from experimental data, it is necessary to have these data over a sufficiently wide interval, of time since integration in (38) is from 0 to ∞ .

To integrate (38) it is necessary first to approximate the experimental results by a suitable function, and for this purpose, we may use not any suitable function, but only those which satisfy equation (36). This condition greatly reduces the type of functions adapted for the purpose. Therefore it is more expedient to use the following method. From (36) it follows that for a very large class of functions $\rho(x)$, the function $\psi(t)$ can be expressed as a series

$$\psi(t) = \sum_{n=0}^{\infty} \frac{a_n n!}{t^{n+1}} \left(1 - e^{-K_0' t} \sum_{m=0}^{n!} \frac{(K_0' t)^m}{m!}\right) \quad (41)$$

It is readily apparent from (40) that resolution (41) corresponds to expressing the function $\rho(E)$ as the series

$$\rho(E) = \frac{1}{RT} \sum_{n=0}^{\infty} a_n K_0' n+1 e^{-(n+1)E/RT}$$

Terminating the series at some term, we obtain for $\psi(t)$ the polynomial

$$\psi(t) \approx \sum_{n=0}^k \frac{a_n n!}{t^{n+1}} \left(1 - e^{-K_0' t} \sum_{m=0}^n \frac{(K_0' t)^m}{m!}\right)$$

For large values of $K_0' t$ the terms containing $e^{-K_0' t}$ can be disregarded, in which case we have

$$\psi(t) \approx \sum_{n=0}^k \frac{a_n n!}{t^{n+1}} \quad (42)$$

On formulating the experimental data as a polynomial in $1/t$ we can determine the coefficients a_n .

The value of K_0' can be determined by means of the formula

$$\ln K_0' = \frac{T_2 \ln t_2 - t_1 m t_1}{T_1 - T_2} + \ln(-\ln \psi) \quad (43)$$

where t_1 and t_2 are points of time corresponding to two equal values $\psi(t) = \psi_1$, determined at temperatures T_1 and T_2 , respectively.

Formula (43) can be derived in the following manner. For the same value of ψ , at different temperatures T_1 and T_2 and some value of the activation energy $E = E^*$, we have the equation

$$\exp[-K_0' e^{-E^*/RT_1} t_1] = \exp[-K_0' e^{-E^*/RT_2} t_2];$$

hence
$$\ln t_1 - \frac{E^*}{RT_1} = \ln t_2 - \frac{E^*}{RT_2}$$

If $T_2 = \infty$, then the same value ψ will be attained at some time t_{∞} , and

$$\ln t_1 - \frac{E^*}{RT_1} = \ln t_{\infty} \quad (44)$$

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Analogously, if $T_1 = \infty$, then

$$\ln t_2 - \frac{E^*}{RT_2} = \ln t_{\infty} \quad (45)$$

From equations (44) and (45) we obtain

$$\ln t_{\infty} = \frac{T_1 \ln t_1 - T_2 \ln t_2}{T_1 - T_2} \quad (46)$$

It follows from equation (28) that when $T = \infty$ and $t_2 = t_{\infty}$, we have

$$\psi = \int_0^{\infty} e^{-K_0 t_{\infty}} \rho(E) dE = e^{-K_0 t_{\infty}} \int_0^{\infty} \rho(E) dE = e^{-K_0 t_{\infty}} \quad (47)$$

Wherefrom it is easy to obtain formula (43) by means of equation (46).

For medium saturations, the second term of (43) can usually be disregarded and then (43) becomes the formula given by Roginskiy:

$$\ln K_0 \approx \frac{T_2 \ln t_2 - T_1 \ln t_1}{T_1 - T_2}$$

Having found the coefficients a_n and K_0' , function $\rho(E)$ is determined as the polynomial

$$\rho(E) \approx \frac{1}{RT} \sum_{n=0}^l a_n K_0'^{n+1} e^{-(n+1)E/RT}$$

If the experimental data yield not $\psi(t)$ but the amount of adsorbed substance $q(t)$, then, from the obvious relation $q = \beta(1 - \psi)$ and (42), we obtain the equation

$$q(t) = \beta - \sum_{n=0}^l \frac{a_n n! \beta}{t^{n+1}}$$

from which, in conjunction with the experimental data, we can determine β and the coefficients a_n .

Under certain conditions, the foregoing method allows us to evaluate the size of the adsorbent's surface from data on adsorption kinetics.

Thus, if $q(t)$ is expressed in number of molecules, then β is equal to the number of molecules on the completely occupied surface. If we know the area S_0 occupied by one adsorbed molecule, the surface S of the adsorbent is equal to $S = \beta S_0$.

A more detailed presentation of the above method will be published elsewhere.

All of the foregoing considerations relative to adsorption kinetics are valid if the pressure of the substance being adsorbed remains constant. Let us now consider the process taking place under varying pressure. The differential equation of adsorption kinetics is (26). Integration of this equation at varying pressure gives

$$1 - \theta = \exp \left[-K_0 e^{-E/RT} \int_0^t p dt \right] \quad (48)$$

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If τ is

$$\tau = \frac{1}{p_0} \int_0^{\tau} p dt$$

where p_0 is the initial pressure of the substance being adsorbed, then equation (48) becomes

$$1 - \theta = \exp \left[-K_0 e^{-E/RT} p_0 t \right] \quad (49)$$

On comparing (49) with (27) it is readily perceived that in the case of varying pressure all the foregoing considerations remain valid if the time t is replaced throughout with the conventional time τ .

Kinetics of Heterogeneous Catalytic Reactions

According to a widely accepted concept, the velocity of a complex multi-stage process, such as a heterogeneous catalytic reaction, is determined by the velocity of the slowest stage component. This controlling stage can be the velocity of the slowest stage component. This controlling stage can be the adsorption of the reaction components on the catalytic surface, or the chemical process occurring on the surface, or the process of desorption of the reaction products, or, finally, the processes of drawing the reacting substances toward or from the surface (diffusion kinetics). An additional factor which complicates, and sometimes radically alters, the kinetic characteristics, is the process of catalyst poisoning, either by reaction products or by extraneous poisons. Among the earliest researches concerned with theories of heterogeneous surfaces, were the investigations of Constable, which dealt with the kinetics of catalytic dehydrogenation of alcohol, and which are now only of historical significance. [16] Studying this process on copper catalysts prepared at different temperatures, Constable discovered that the pre-exponential factor increases with increasing activation energy of the catalyst. In an attempt to explain this observation, Constable suggested the existence, on the catalyst surface, of points having different activity values, at which points the reaction actually takes place. Having postulated the interrelation of the activity of such points with the deviations Δd from interatomic distances, and adopting for the probability $\omega(\Delta d)$ of these deviations, Gauss' law of errors

$$\omega(\Delta d) \propto e^{-A(\Delta d)^2}$$

where A is a constant, Constable obtained for a number of active points characterized by a value of activation energy E the expression $A'' e^{hE}$, where the constants A'' and h depend on the nature of the catalyst and on the conditions under which it is produced. The reaction velocity at an active point having a given value E is equal to

$$W_E = K_0 e^{-E/RT} \theta$$

If K_0 and θ (the degree of saturation by the reactant) are assumed to be constant at all active points, which is most arbitrary, the velocity on the entire surface is equal to

$$W = K_0 \theta A'' \int_{E_1}^{E_2} e^{-E/RT} e^{hE} dE = K_0 \theta A'' \frac{e^{(h-1/RT)E_2} - e^{(h-1/RT)E_1}}{h-1/RT}$$

In view of the magnitude of E_2 , the upper limit of the activation energy value, terms containing E_2 in the exponent ($h < 1/RT$) can be disregarded, which gives the expression,

$$W = B \frac{e^{hE_1} e^{-E_1/RT}}{1/RT - h}$$

that is, the desired dependency between the pre-exponential factor and the energy of activation.

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The kinetics of catalytic reactions and processes of catalyst poisoning on a heterogeneous surface have been studied in their most general aspects by Roginskiy. [29, 36] We shall discuss here some of the general considerations, primarily in the light of Roginskiy's work.

1. The reaction velocity is determined by the adsorption activation of the components.

a. In the absence of poisoning. The velocity of the chemical process on the surface and the velocity of desorption of the products substantially exceed the adsorption velocity, which, in this instance, is equal to

$$W = c_x \nu_x \int_{E_1}^{E_2} K_0 e^{-E/RT} \rho(E) dE = K_0 e^{-E_{av}/RT} \nu_x c_x \quad (50)$$

$[E_{av} = E_{average}]$

where c_x is the concentration of the substance, the adsorption of which constitutes the controlling stage of the reaction; ν_x is the number of p particles of this substance which form the activated complex (order of adsorption by activation); and E is the adsorption activation energy. From (50) it is apparent that, in this case, the heterogeneous surface displays properties which reproduce those of a homogeneous surface.

b. The reaction products are irreversibly adsorbed on the surface. The reaction kinetics (assuming c_x to be constant) coincides with that of the activated adsorption, described above. In the absence of redistribution, or, with redistribution and with antibiotic E (adsorption activation energy, of the component X), and Q_p (adsorption heat of the poisonous reaction product), the velocity W , in view of (26) and (27), is equal to

$$W = c_x \nu_x \int_{E_1}^{E_2} K_0 e^{-E/RT} \rho(E) [1 - \theta(E)] dE = c_x \nu_x \int_{E_1}^{E_2} K_0 e^{-E/RT} \exp[-K_0 t e^{-E/RT} \cdot c_x^{\nu_x}] \rho(E) dE \quad (51)$$

It is apparent from (51) that in this case the kinetic equations are of a type $\phi(t) = a \cdot e^{-kt}$ and $\phi(t) = At^\gamma$ which are characteristic of activated adsorption.

c. In the presence of redistribution on the surface and in the absence of a dependence between adsorption activation energy (of the component X) and the heat of adsorption (of the reaction product). In such a case, we obtain for the velocity an expression analogous to (29), namely:

$$W = c_x^{\nu_x} K_0 e^{-E_{min}/RT} (1 - \phi) = c_x^{\nu_x} K_0 \exp\left[-\frac{E_{min}}{RT} - K_0 c_x^{\nu_x} t e^{-E_{min}/RT}\right] = K'(T) e^{-K'(T) t}$$

Here also the properties of a homogeneous surface are, thus, reproduced.

In the case of a symbatic variation of E and Q_p , we have further:

$$W = K_0 (c_x^{\nu_x} \rho(E_{min})) e^{-E_{min}/RT} \quad (53)$$

d. The reaction product is reversibly adsorbed on the surface. The degree of saturation of the surface by the poisonous reaction product in the case of a homogeneous surface is equal to

$$\theta_p = \frac{\pi}{\pi + b_p} \quad (54)$$

where π is the volume concentration of the product.

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In the absence of a functional relation between E and Q_r , the reaction velocity is equal to

$$W = C_x^{V_x} K_o e^{-E_{min}/RT} (1 - \phi_r) \quad (55)$$

where ϕ_r is the total fraction of saturation by the poisonous product of the total heterogeneous surface, which is equal to

$$\phi_r = \int_{Q_r}^{Q_{r2}} \frac{\pi}{\pi + b_r} \rho(Q_r) dQ_r \quad (56)$$

Equation (55) suggests the corresponding equation, in the case of a homogeneous surface

$$W = C_x^{V_x} K_o e^{-E/RT} (1 - \theta_r)$$

which differs, however, in that the dependence of the fraction of saturation by the poison upon π is expressed not by the Langmuir isotherm (54), but by the formula (56). In the case of an exponential form of $\rho(Q_r)$, on applying formula (17), we obtain

$$W = C_x^{V_x} K_o e^{-E_{min}/RT} (1 - a\pi^{\delta})$$

If Q_r and E are sybatic, the presence of the poison does not affect the kinetics, except at the highest saturations, when the poison finally reaches the most active areas (those having minimum E) of the controlling band, whereupon an abrupt (exponential) decrease of the velocity takes place (Figure 7). Finally, when Q_r and E vary antitabically, the poison occupies, from the start, the most active areas, i.e., those having minimum activation energy. In such a case, the form of dependence between E and Q_r is of substantial significance.

Let us assume, as it is frequently done, that

$$Q_r = Q_o - \beta E \quad (57)$$

The reaction velocity on the area with a given value $E = E_i$ is equal to

$$\begin{aligned} W_i &= K_o C_x^{V_x} e^{-E_i/RT} \left(1 - \frac{\pi}{\pi + b_o \exp(-Q_i/RT)} \right) \\ &= K_o C_x^{V_x} \frac{b_o}{\pi \exp[(E_i + Q_o)/RT] + b_o \exp[E_i/RT]} \end{aligned}$$

or, on taking into consideration (57), we have

$$W_i = \frac{K_o b_o C_x^{V_x}}{\pi \exp[Q_o + (1 - \beta)E_i]/RT] + b_o \exp[E_i/RT]} \quad (58)$$

If $\beta < 1$ the maximum velocity will occur on areas having minimum E_i values, in spite of the fact that on these areas there is present the greatest amount of the poison. We have thus

$$W_{max} = K_o C_x^{V_x} b_o \exp\left[-\frac{[Q_o + (1 - \beta)E_{min}]}{RT}\right] \cdot \frac{1}{\pi + b_o \exp[-(Q_o - \beta E_{min})/RT]}$$

or, disregarding $b_o \exp[-(Q_o - \beta E_{min})/RT]$ as compared with π (Q_o is a large quantity), and setting $Q_o + (1 - \beta)E_{min} = E'$ we obtain

$$W \approx \frac{K_o C_x^{V_x} e^{-E'/RT}}{\pi} \quad (59)$$

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If, on the other hand, $\beta > 1$, then the expression (58) has a maximum, which we can determine by setting $\frac{dW}{dE}$ equal to zero and solving the resulting equation for E_{opt} :

$$E_{opt} = \frac{1}{\beta} (Q_0 - RT \ln \frac{b_0}{\pi(\beta-1)})$$

On substituting the expression so obtained in (58), we have

$$W_{max} = \frac{K_0 b_0^{1/\beta} (\beta-1) e^{-Q_0/\beta RT} C_x^{\nu_x}}{(\beta-1)^{1/\beta} \beta + \pi^{1/\beta}} = \frac{K_0' e^{-Q_0'/RT} C_x^{\nu_x}}{\pi^{1/\beta}}$$

In this case, therefore, as the poison is being adsorbed, the controlling band of graph $f(E)$ will move toward higher E values (Figure 8).

The expression (60) suggests Langmuir's dependence in the case of poisoning by blocking on a homogeneous surface, but differs from it, however, in that the poison concentration is of the fractional order $1/\beta$.

The above-cited examples do not, by any means, exhaust the multifarious aspects of kinetics on heterogeneous surfaces in the presence of catalyst poisoning; not even in the particular case where the reaction is controlled by the adsorption stage of the process. Poisoning, by extraneous products, of a catalytic reaction controlled by the chemical process on the surface, or by the desorption stage, is governed by distinct and interesting laws. (It can be readily ascertained that the interdependence of reaction velocity and concentration of the poison, set out in section c, are applicable not only in the case of a reaction controlled by the adsorption stage, with formation of poison containing reaction products. They relate also to reactions controlled by desorption and by the chemical process on the surface, as well as to poisoning by extraneous poisons; provided that the conditions of (57) are satisfied.) However, we shall not here make a detailed analysis of these problems [see 29, 36] but consider next the reactions controlled by the processes occurring on the surface.

2. The reaction velocity is controlled by the chemical process occurring on the surface.

The velocity of the reaction taking place on the surface



where A_1, A_2, \dots are the reactants, and Y is the reaction products, is given in the case of a homogeneous surface by the equation

$$W = K_0 e^{-E/RT} \theta_1^{n_1} \theta_2^{n_2} \dots \quad (61)$$

where E is the actual activation energy (that is, the heat of formation of the activated complex, computed on the basis of the zero energy level of the adsorbed particles) and $\theta_1, \theta_2, \dots$ the degree of surface saturation by the respective reactants. This equation can also be formulated as

$$W = K_0' e^{-Q^*/RT} p_1^{n_1} p_2^{n_2} \dots (1 - \theta_1 - \theta_2 - \dots)^{n_1 + n_2 + \dots} \quad (62)$$

where Q^* is the apparent activation energy, that is, the heat of formation of the activated complex, computed on the basis of the zero energy level of the particles in the gaseous phase, with

$$Q^* = E - n_1 Q_1 - n_2 Q_2 - \dots \quad (63)$$

where Q_1, Q_2, \dots are the adsorption heats of the reactants, and p_1, p_2, \dots are their partial pressures.

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On a heterogeneous surface, the different areas (zones wherein the activated complex is disposed) are characterized by different values of Q_1, Q_2, \dots and of E or Q^* , and the reaction kinetics will be determined by the nature of the dependence between these quantities on passing from one area to another. Let us consider some of these specific variants.

1. Let us suppose that with an increase of the activation energy E , in a reaction involving only one kind of particles, the heat of adsorption decreases from one area to another (antibaticity). Then the areas having minimum E values will be those of maximum adsorption heat. Because of the sharp variation in the reaction-velocity constant, with activation energy, and because of the fractions of surface saturation by the reacting substance with the adsorption heats, the reaction velocity on the entire surface will be practically equal to the reaction velocity on the areas having minimum E and maximum Q values. For not too low pressures, θ in formula (61) can, for practical purposes, be taken equal to one (since the areas having the greatest adsorption heats are involved), and the reaction velocity on the entire surface is given by the equation

$$W = K_0 e^{-E_{min}/RT} \cdot \rho(E_{min}) = K_0' e^{-E_{min}/RT}$$

which is of zero order; thus the energy of activation is independent of the saturation.

For very low pressures, when θ can no longer be considered equal to one, we have the following relation:

$$W = K_0 e^{-E_{min}/RT} \cdot \frac{P/b_{min}}{1+P/b_{min}}$$

which is derived from (61). In this case, therefore, the kinetics observed on a heterogeneous surface will be that characteristic of a homogeneous surface.

2. Let us now consider when, with increasing activation energy E , the adsorption heats of the reacting substances also increase (sympaticity). In this instance, the areas having minimum activation energies are also those having minimum adsorption heats. If the activation energy changes more rapidly than the heat of adsorption, for example, in accordance with $E = E_0 + \alpha Q$, where $\alpha > n$ (see formula 63), the reaction velocity will be determined by the process taking place on areas with low activation energy and low adsorption heat. Since on these areas $\theta_1, \theta_2, \dots$ are very small, they can be disregarded in formula (62), in comparison with unity, and we then have

$$W = K_0' e^{-Q_{min}^*/RT} p_1^{n_1} p_2^{n_2} \dots$$

i.e., kinetics similar to homogeneous kinetics.

If, however, the activation energy changes more slowly than the adsorption heats, the areas of minimum activation energy will contain too few reacting molecules, and maximum reaction velocity will occur on areas with optimum relation between E and Q . In contradistinction to all other cases, in this instance the controlling band of the graph $\rho(E)$ will no longer be stationary, but will move with increasing pressure of the reacting substances toward larger E values. We can illustrate this rule in the case of a monomolecular reaction mechanism on a catalyst, for which the dependence of activation energy upon adsorption heat of reactant is expressed by the formula

$$E = E_0 + \alpha Q \quad (64)$$

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According to (61) and (64), the reaction velocity on an area with an adsorption heat Q is given by the equation

$$W = K_0 e^{-E_0/RT} e^{-\alpha Q/RT} \cdot \frac{p}{p + b_0 e^{-Q/RT}} = K_0 e^{-E_0/RT} \frac{p}{p e^{\alpha Q/RT} + b_0 e^{[(\alpha-1)Q]}}$$

If $\alpha \gg 1$, the maximum reaction velocity will occur when Q has the lowest value, and the reaction velocity on the entire surface will be equal to the reaction velocity on areas with minimum Q ,

$$W_{max} = K_0 e^{-E_0/RT} e^{-\alpha Q_{min}/RT} \cdot \frac{p}{p + b_0 e^{-Q_{min}/RT}}$$

or, on disregarding p in comparison with $b_0 e^{-Q_{min}/RT}$ in the denominator, we have

$$W_{max} = K_0 \frac{p}{b_0} e^{[-E_0 + (\alpha-1)Q_{min}]/RT} = K'_0 e^{-Q^*_{min}/RT} \cdot p$$

If $\alpha < 1$, then on determining the maximum velocity in the usual manner, we obtain the optimum value of Q ,

$$Q_{opt} = -RT - \ln \left[\frac{\alpha}{1-\alpha} \cdot \frac{p}{b_0} \right]$$

and the reaction velocity on the entire surface is equal to

$$W = K'_0 \exp \left[-\frac{E_0 - \alpha RT \ln \left(\frac{\alpha p}{(1-\alpha)b_0} \right)}{RT} \right] \cdot \frac{p}{p + \frac{\alpha}{1-\alpha} p} = K'_0 e^{-E_0/RT} \cdot p$$

that is, a fractional order reaction ($\alpha < 1$) characteristic of symbatic E and Q will take place.

3. Finally, if no functional relation exists between activation energy and adsorption heats, that is, to a given value E correspond any values Q_1, Q_2, \dots , the controlling band will again be situated in the region of minimum E . For low saturation, we have $(1 - \theta_1 - \theta_2 - \dots) \approx 1$

$$\text{and } W = K_0 e^{-Q^*_{min}/RT} \cdot p_1^{n_1} \cdot p_2^{n_2} \dots$$

In general, however, the velocity will be equal to

$$W = K_0 e^{Q^*_{min}/RT} p_1^{n_1} p_2^{n_2} \dots (1 - \phi_1 - \phi_2 - \dots) = K'_0 e^{-Q^*_{min}/RT} p_1^{n_1} p_2^{n_2} \dots \psi$$

The value of the free surface ψ can be determined by means of the Roginskiy and Todes formula for the adsorption of gaseous mixtures. [33]

4. The reaction of velocity is determined by the desorption of the reaction products.

Without expounding in detail the recurring regularities which take place in this instance, we can cite as an example the analysis of kinetics of the catalytic decomposition of ammonia, studied by Temkin and Pyzhev [38], whose work embodied the first successful application of the concept of heterogeneous catalyst surface to a complex technological process. According to the experimental results of Winter [39], the decomposition velocity of ammonia on iron is given by the equation:

$$W = K \frac{p_{NH_3}}{p_{H_2}^{1.5}}$$

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In accordance with the viewpoint held by most investigators, the decomposition velocity is determined by the desorption process of the nitrogen formed by dissociation of ammonia on catalyst.

Consequently, the nitrogen adsorbed on the surface will be in equilibrium with the hydrogen and the ammonia (but not with the nitrogen) of the gaseous phase. If $p_{N_2}^*$ is used to designate the nitrogen pressure (fictitious), which would correspond to the actual saturation of the surface ϕ_{N_2} at equilibrium, then in accordance with the reaction $2 NH_3 = N_2 + 3 H_2$, we have the equation

$$p_{N_2}^* = K_{equil} \frac{p_{NH_3}^2}{p_{H_2}^3}$$

Assuming, as did Temkin and Pyzhev, that the surface of the catalyst is characterized by uniform distribution in adsorption heats, we obtain, on applying formula (12),

$$\phi_{N_2} = C_1 \ln(a p_{N_2}^*) = C_1 \ln \left(a K_{equil} \frac{p_{NH_3}^2}{p_{H_2}^3} \right) = C_1' + c_2 \ln \frac{p_{NH_3}^2}{p_{H_2}^3}$$

If it is further assumed that equation (31) is applicable in the given case, that is, antibatic adsorption heat and activation energy, then the desorption velocity obtained by means of formula (34a) will be

$$W = K_0'' e^{-h\phi_{N_2}} = K_0' \exp \left[h C_1' + h c_2 \ln \frac{p_{NH_3}^2}{p_{H_2}^3} \right] = K \left(\frac{p_{NH_3}^2}{p_{H_2}^3} \right)^{h c_2}$$

If $h c_2 = Y_2$, we have the desired relation, namely:

$$W = K \left[\frac{p_{NH_3}^2}{p_{H_2}^3} \right]^{1/2} = K \frac{p_{NH_3}}{p_{H_2}^{1.5}}$$

By analogous reasoning Temkin and Pyzhev obtained, for the velocity of the synthesis, the equation

$$W' = K_2 \frac{p_{N_2}^{1.5} p_{H_2}}{p_{NH_3}}$$

(The discussion of the problem by Temkin and Pyzhev and some of the formulas have been altered somewhat, in order to conform to the form of presentation adopted in the present article.)

Of considerable importance is the problem of determining the distribution function in activation energies of a catalytic reaction from experimental data relative to kinetics of such a reaction.

The solution of this problem is complicated by the fact that if several areas having different activation energy are concurrently active on the surface, only the most active areas (the controlling band) will affect, in practice, the total kinetics. Therefore, the distribution function can be found, on the basis of kinetics, only in the case where, for one reason or another (for instance as a result of catalyst poisoning), in the course of the reaction some areas are eliminated in a definite sequence. If we assume that such elimination of areas occurs in the order of increasing activation energy, and further, that a monomolecular reaction is involved, of a substance so readily adsorbed that the amount of reactant by volume can be disregarded, and if we can consider it as being present in toto on the surface of the catalyst (layer reaction), then the reaction velocity on a homogeneous area, in the absence of distribution of the adsorbed substance, is equal to

$$-\frac{d\theta}{dt} = K_0 e^{-E/RT} \cdot \theta$$

Hence, the degree of saturation with respect to the substance which has not reacted at the time t is equal to

$$\theta(t) = \theta_0 \exp \left[-K_0 e^{-E/RT} \cdot E \right]$$

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For the entire heterogeneous surface, in view of (5), we have the equation, (if θ_0 is the same for all areas),

$$\phi(t) = \theta_0 \int_{E_1}^{E_2} \exp[-K_0 e^{-E/RT} t] p(E) dE \quad (65)$$

where ϕt is the degree of saturation by the unreacted substance on the total surface, and $p(E)$ the distribution function in activation energies E of the catalytic reaction.

Comparing equations (65) and (28) we see that they are formally identical, and consequently, in the given case, to determine $p(E)$ we may utilize all the above methods adapted for determining the distribution function by the adsorption activation energies.

Comparing the Theory of Heterogeneous Surfaces
and the Theory of Interaction of the Adsorbed Particles

As was previously mentioned, a rejection of Langmuir's postulate of surface homogeneity is not the only means of evolving the theory of active surfaces. A number of authors developed a theory of adsorption taking into consideration the interaction of adsorbed particles, while retaining the postulate of surface homogeneity. From a strict viewpoint, these authors were just as successful as the proponents of heterogeneity in explaining the experimentally observed recurring regularities by assuming one or another premise as to the general law governing the mutual action of the particles. P. P. Volkenshteyn [37], shows in his publication a table of the same isotherms which were derived by Roginskly on the basis of the concept of heterogeneous surfaces and indicates the nature of the interaction of the adsorbed particles on the basis of which these isotherms are obtained. The same author also shows the methods for determining the rule which controls such interactions, from a given isotherm, and vice versa.

It would appear that the theory based on the interaction of molecules, is fully as authoritative as that of heterogeneous surfaces. However, a number of substantial objections can be cited against the former. According to Volkenshteyn, the adsorption isotherm can be formulated as follows:

$$KT \ln \frac{1-\theta}{p} - \Delta\phi = KT \ln \frac{b}{p} \quad (66)$$

wherein $\Delta\phi$ is the energy of interaction of the adsorbed molecules. For low orders of saturation the interaction is slight, that is, for $\theta \rightarrow 0, \Delta\phi \rightarrow 0$. On the other hand, at high saturation this energy approaches a certain constant value so that $0 < \Delta\phi < const$

On rewriting (66) as:

$$\ln \frac{1-\theta}{p} = \ln \frac{b}{p} + \frac{\Delta\phi}{KT} \quad (67)$$

the term b/p increases without bound with decreasing pressure. At the same time, $\Delta\phi/KT$ decreases. Hence, at low pressures (67) becomes the isotherm of Langmuir, that is, at low pressures the Langmuir isotherm holds, irrespective of the nature of the law governing the interaction. The widest deviations from the isotherm of Langmuir must occur when $p \approx b$ that is, for medium pressures. Experimentally, however, the very first points of the isotherm for low pressures frequently do not satisfy Langmuir's equation; and conversely, they are in agreement therewith at medium and high pressures. [3, 4, 21] On the other hand, on heterogeneous surfaces and in the absence of interaction, as shown by

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Zel'dovich [21] in the case of an exponential distribution in adsorption heats, it is precisely at the low pressures that the theory requires the greatest deviation from Langmuir's relation. A parabolic isotherm (2), is obtained by Zel'dovich when $p \ll b_0$. At medium and high pressure ($p > b$), on developing $\frac{1}{p+b}$ of (4) as a series and integrating, Zel'dovich obtains the expression

$$\phi(p) = 1 - \frac{b_0 \gamma + 1}{\gamma + 1} \cdot \frac{1}{p} + \frac{b_0 \gamma + 2}{\gamma + 2} \cdot \frac{1}{p^2} \dots$$

which differs from the developed Langmuir function only in the coefficients of higher powers of $1/p$.

Furthermore, in order to explain a parabolic isotherm on the basis of particles interaction, it is necessary to assume the following improbable correlation [37]

$$\Delta \phi = \alpha_0 \ln \left(\alpha_1 + \frac{\alpha^2}{r^2} \right)$$

where r is the distance between particles. This relation differs widely from the usual laws of interaction, according to which the energy decreases with the distance as $1/r$ ($1 < \beta < 6$) and even as e^{-ar} .

Thus, the most frequently encountered empirical conditions are more readily explainable on the basis of the concept of heterogeneous surface than by interaction of particles.

A series of recently obtained experimental data also substantiates the energetic heterogeneity of adsorbent surfaces. Roginsky and Keier [40], on studying the adsorption of hydrogen on charcoal, obtained the following results by means of the "isotope method," first proposed by these authors.

If at first light hydrogen (H_2) and then heavy hydrogen (D_2) are adsorbed on the same batch of charcoal, on subsequent desorption the gases are desorbed in the reversed order, that is, first the heavy hydrogen and then the light hydrogen. If the order of adsorption is reversed, that is, D_2 is adsorbed first, followed by H_2 , then the order of desorption is also reversed. This phenomenon cannot be explained if it is assumed that the surface is homogeneous. On the other hand, if the surface is heterogeneous with respect to adsorption heats, it is readily apparent that the first adsorbed gas occupies the areas having higher adsorption heats and, consequently, is less readily desorbed; and conversely, the last adsorbed gas occupies the areas of minimum adsorption heat and is more readily desorbed.

Taylor and Shou Chu-liang [41] have found that if, in the process of activated adsorption of hydrogen on zinc oxide, the temperature is raised rapidly, then a partial desorption of the gas occurs at first, after which the adsorption gradually increases again, reaches its former value, and then continues to increase further.

A similar process was observed by the present author on adsorbing carbon monoxide on nickelous oxide (unpublished data). This phenomenon is readily explainable on assumption of surface heterogeneity. Since a heterogeneous surface comprises areas of different adsorption heat and of different adsorption activation energy, a portion of these areas is practically completely occupied while the remainder is practically not occupied at all. With increasing temperature, on the occupied areas partial desorption takes place, inasmuch as the amount of adsorptive present on these areas now exceeds the amount in equilibrium at the prevailing temperature. On the other hand, on the areas which were not occupied prior to the temperature rise because of excessive activation

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energy of these areas, increasing temperature causes increasing adsorption because of an increase of the adsorption velocity. Thus, the temperature change causes a peculiar, abrupt passage of the adsorptive from one group of areas to another through the gaseous phase.

In conclusion, it must be noted that both theories share the shortcoming of not being founded on an irrefutable physical pattern, and the final solution of the question as to whether one may disregard the mutual interaction of the particles, as well as that surface heterogeneity, will probably be attained when a rigorous physical theory of adsorption has been postulated and sustained.

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[Appended figures follow.]

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[Note: $K\pi$ means 'controlling band'.]

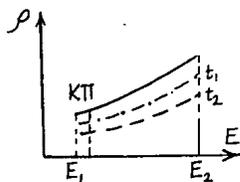


Figure 4. Adsorption Kinetics in Absence of Dependence of E on Q. (The area below curve t_1 is portion of free surface to moment t_1 ; area under curve t_2 is portion of free surface to moment t_1 ($t_2 > t_1$).

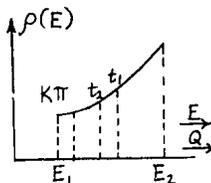


Figure 5. Adsorption Kinetics for Symbatic E and Q. (The area under the curve from ordinate of E_1 to ordinate corresponding to t_1 and t_2 is the portion of the occupied surface to moments t_1 and t_2 .)

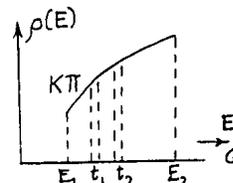


Figure 6. Adsorption Kinetics for Antibatic E and Q. (The area under the curve from ordinate E_1 to the ordinate corresponding to t_1 and t_2 is the portion of the busy surface to moments t_1 and t_2 ($t_2 > t_1$).

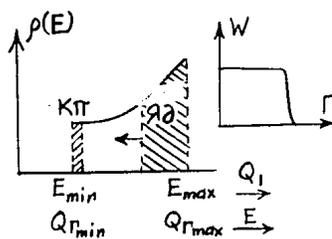


Figure 7. Poisoning of the Catalyst During Symbaticity of the Heat of Adsorption of the Poison $Q\Gamma$ and Activation energy of Adsorption E. W: velocity of the reaction Γ : quantity of poison adsorbed

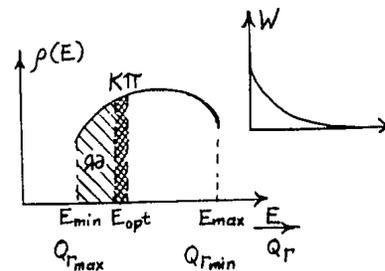


Figure 8. Poisoning of the Catalyst for Antibaticity of $Q\Gamma$ and E. E_{opt} : energy of activation of parts with maximum velocity of reaction.

[Note: 'QΓ' means poison.]

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